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Pure phase orthorhombic $MgTi_2O_5$ photocatalyst for H_2 production

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Undesirable phase transformation was overcame and pure phase orthorhombic $MgTi_2O_5$ nanocrystals were facilely prepared. Two factors of the concentration of metal ions and reaction temperature were found to affect the phase transformation of magnesium titanantes. The as-prepared pure phase $MgTi_2O_5$ nanocrystals possessed of high crystallinity and 20 nm in diameter. They exhibited excellent photocatalytic hydrogen production activity(418 $\mu mol \cdot h^{-1}$), and high apparent quantum efficiency (62.5% at 313 nm and 50.6% at 365 nm, respectively). Significantly, the "solar-to-hydrogen" efficiency of 0.52% was obtained. This may be attributed to the pure phase crystals and large surface area favored charge transfer and promoted the photo-induced charge separations which is proved by photoelectrochemical measurements.

Introduction

Owing to the fantastic effect of semiconductor and powerful solar energy, the dream of splitting water to hydrogen has been come ture.[1] However, limited by the photocatalyst materials, complex thermal/dynamics reactions and the ambiguous mechanism, the efficiency of photocatalytic H_2 production is still very low, far from the requirement of industrialization. How to solve these thorny issues become challenges.[2, 3]

Alkali titanates with the formula of $M_2Ti_nO_{2n+1}$ have unique layered and ilmenite or tunnel-like crystal structure, which have attracted increasing attention due to their more negative conduction band and high photocatalytic activities.[4, 5] Hereinto, $MgTi_2O_5$ possesses suitable electronic structures and conduction/valence band positions, which matches well with the redox potential of water into hydrogen and oxygen molecules. $MgTi_2O_5$ has theoretical band gap energy of approximately 3.4 eV, and contains the Ti^{4+} of the d^0 metal which has the potential activity of water splitting.[6] However, pure orthorhombic phase $MgTi_2O_5$ are very hard to prepare because the two main magnesium titanates of $MgTiO_3$ and $MgTi_2O_5$ are associated minerals.[7-10] These two phases transformation may be caused by the possible crystallography incompatibilities, which may cause undesired secondary phases often happened in conventional solid state method to prepare magnesium titanates.[11] However, pure phase materials are beneficial to photocatalysis for the reason of the reduction of impurities and lead to fast charge transport from bulk to surface. Moreover, synthesis of pure phase titanates is significant to not only the property themselves but also to the inside study of their electronic energy structure. M. Morimoto reported the synthesis of uniformly porous $MgTi_2O_5$ with narrow pore-size distribution at 1000-1200°C and they show excellent thermal expansion behavior.[12] Recently, Deng and Chen *et al.* prepared a novel hybrid $MgTi_2O_5$–C nanocomposite from an in situ carbonization process of a cheap single molecule precursor with unique morphology and exhibited promoted lithium ion batteries property.[13] So, developing methods to prepare pure phase $MgTi_2O_5$ is significant to enhance their property.

Generally speaking, if the phase transformation could be controlled or the MO_6 units are "fixed", pure phase magnesium titanates may be prepared. Luckily, some works had been demonstrated that the concentration of metal ions could affect the phases of the products.[14, 15] Moreover, it was found in our previous works that parts of bivalent metal are easy to cooperate with some organic ligands (ethylene glycol) to form metal glycolates. Metal oxides or ilmenites were prepared by further calcinations. This means pure phase $MgTi_2O_5$ would be prepared through fixed Mg^{2+} and Ti^{4+} by ethylene glycol and then calcinations.

Hence, we report the facile synthesis of pure phase $MgTi_2O_5$ nanocrystals for H_2 production. Different to the traditional method, we develop organic ligand coordinated polymerization method. Ethylene glycol (EG) acts as ligands to cooperate Mg^{2+} and Ti^{4+} to form MgO_6 and TiO_6 units and linked by EG that could fix the cation distortion to avoid the phase transformation and to form pure phase $MgTi_2O_5$ when calcined in air.

Experimental

Materials

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Analytical grade $Mg(CH_3COO)_2{\cdot}4H_2O$, $Ti(OC_4H_9)_4$, ethanol, methanol and ethylene glycol. All of the reagents and solvents were used as received without further purification. Distilled water was used throughout. For the preparation of pure phase $MgTi_2O_5$, 0.0670 g $Mg(CH_3COO)_2{\cdot}4H_2O$ and 0.1062mL $Ti(OC_4H_9)_4$ were dissolved in 30 mL ethylene glycol, then the solution was stirred at room temperature for about 30 min. Subsequently, the obtained products were collected by means of centrifugation, washed with ethanol for three times, and dried in air at 80 °C for 4 h, and finally sintered at 600 °C for 2 h in air, with a constant heating rate of 2 °C min^{-1}. The productivity of products was about 45%. For easy distinguish, pure phase $MgTi_2O_5$, mixed phase $MgTiO_3/MgTi_2O_5$ and commercial $MgTi_2O_5$ were donated to PMT, MMT and CMT, respectively.

Characterization

The crystal structure was analyzed by a X-ray powder diffraction (XRD) patterns were obtained by Bruker D8 Advance diffractometer by using Cu Kα radiation (λ = 1.5406 Å, 40 kV, 40 mA). The size and morphology of the final products were investigated by scanning electron microscopy (SEM, Hitachi, S-4800) and transmission electron microscopy (TEM, JEOL, JEM-2010). Nitrogen adsorption-desorption isotherms were collected using a Tristar II 3020 surface area and porosity analyzer (micromeritics). The pore size distribution plots were obtained by the Barret-Joyner-Halenda (BJH) model. UV-Vis absorption spectra were determined by a UV-Vis spectrophotometer (Shimadzu UV-2550, Tokyo, Japan). Raman measurements were performed with a Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm. The laser beam was focused with a 50 × objective lens to a ca. 1μm spot on the surface of the sample. X-ray Photoelectron Spectroscopy (XPS) were tested using a Kratos-AXIS ULTRA DLD apparatus with Al(Mono) X-ray source, and the binding energies were calibrated with respect to the signal for adventitious carbon (binding energy = 284.6 eV).

Photocatalytic H_2 production experiment

The photocatalytic H_2 evolution from water was conducted in an online photocatalytic hydrogen production system (AuLight, Beijing, China, CEL-SPH2N). A powder sample of the catalyst (0.1 g) was suspended in a mixture of 80 mL distilled water and 20 mL methanol in the cell by using a magnetic stirrer. Pt-loaded photocatalysts were prepared by known standard method of in situ photo-deposition method. For this, the photocatalyst powder was added to an aqueous methanol solution containing a required amount (1 wt% of Pt) of H_2PtCl_6. The solution was illuminated for 3 h under Xe lamp with AM 1.5 filter (AuLight), filtered, and then dried in a static oven at 80-100 °C. Before the reaction, the mixture was deaerated by evacuation to remove O_2 and CO_2 dissolved in water. The reaction was carried out by irradiating the mixture with UV light from a 300 W Xe lamp with a 300-390 nm reflection filter which means the wavelength of light is approximately 300-390 nm. Gas evolution was observed only under photo-irradiation, being analyzed by an online gas chromatograph (SP7800, thermal conductivity detector, molecular sieve 5 Å, N_2 carrier, Beijing Keruida Limited, Beijing, China).

Photoelectrochemical measurement

Photocurrent measurements were performed using a three-electrode configuration, with PMT, MMT and CMT films as the working electrode, saturated Ag/AgCl as the reference electrode, and platinum foil (3 × 2 cm) as the counter electrode. The working electrode films were prepared by doctor-blade method, using a thin glass rod to roll a paste on FTO to form a film (2 × 1 cm). The paste was prepared by stirring 0.2g photocatalyst powders in 0.5 mL ethanol for at least 24 h. The films were annealed at 400 °C (ramp of 1 °C min^{-1}) for 1 h to make them firm enough. Electrochemical impedance spectroscopy (EIS) measurements were performed in the dark and under visible light illumination (λ > 400 nm) in 1 M NaOH solution at open circuit voltage over a frequency range from 10^5 to 0.05 Hz with an AC voltage at 5 mV. The Mott-Schottky plots were obtained at a fixed frequency of 1 kHz in the dark.

In addition, all the data in this work, especially the photocatalytic activities and electrochemical measurement, are tested for at least three times to confirm the reproducibility, for scientifically and scrupulously treating to our work.

Results and discussion

Different controlling experiments were done to prepare pure phase $MgTi_2O_5$ (PMT). As shown in Table S1, when the polymerization temperature is low, only TiO_2 is the final product. This displays that the cooperation ability of Mg^{2+} and Ti^{4+} could be influenced by reaction temperature. We can also learn that the concentration affect the final products. Pure phase $MgTi_2O_5$ could only synthesize at a low concentration and suitable polymerization temperature (17 °C). The more EG ratio (lower concentration), the more EG molecule polymerized in the metal glycolate that result in the strong fixation of MO_6 and TiO_6 units.[16]

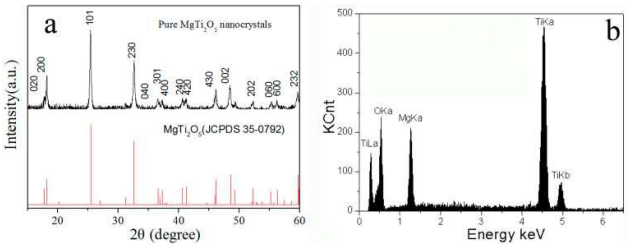
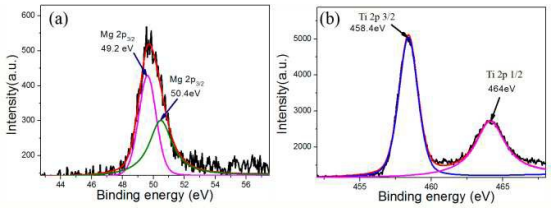


Figure 1. XRD pattern (a) and EDS analysis(b) of pure phase $MgTi_2O_5$ (PMT).

The pure phase could be proven by XRD patterns in Figure 1a, that all the diffraction peaks can be indexed to the pure orthorhombic phase $MgTi_2O_5$ (JCPDS 35-0792). No other impurity peaks such as TiO_2, $MgTiO_3$ and Mg_2TiO_4 were detected. The XRD patterns of samples synthesized by other condition are mixed-phase $MgTi_2O_5/MgTiO_3$ (MMT) that rhombohedral phase $MgTiO_3$ (JCPDS 06-0494) emerged (as

shown in Figure S1). X-ray Energy Dispersive Spectrometer (EDS), in Figure 1b show that sample of PMT contain three elements of Mg, Ti and O. Raman spectrum in Figure S2 gives another evidence of $MgTi_2O_5$ nanocrystals, that is the Raman shift at 661 cm^{-1} and 797 cm^{-1} may be contributed to the vibrations of O atoms and 159 cm^{-1}, 218 cm^{-1} and 266 cm^{-1} may be contributed to the antisymmetric breathing and twisting vibrations of the O octahedral, according to the previous works.[17, 18]



(c)

Peak	Atomic Mass	Atomic Conc %	Mass Conc %
O1s	15.999	54.81	40.80
Ti 2p	47.878	17.60	39.20
Mg 2p	24.312	8.02	9.07

Figure 2. High resolution XPS of Mg (a) and Ti (b) and element analysis (c) of PMT.

XPS in Figure 2 demonstrate that Mg and Ti are +2 and +4 without alterable valence state, and the atom ratios of them are also approximately two. According to the results of XRD and the assistant of EDS and XPS, it could be confirmed that pure orthorhombic phase $MgTi_2O_5$ were successfully prepared.

The optical absorptions of the pure $MgTi_2O_5$ nanocrystals and commercial $MgTi_2O_5$ were conducted with a UV-vis absorption spectrometer, as shown in Figure S3a. Obviously, both the PMT and CMT show the photoabsorption in the UV light region ($\lambda < 400$ nm). It should be noticed that there are some impurities of CMT, which is consistent with the results of XRD (Figure S3b). The band gaps (Eg) of the pure $MgTi_2O_5$ nanocrystals and commercial $MgTi_2O_5$ were calculated to be about 3.45 eV from the onset of the absorption edges.

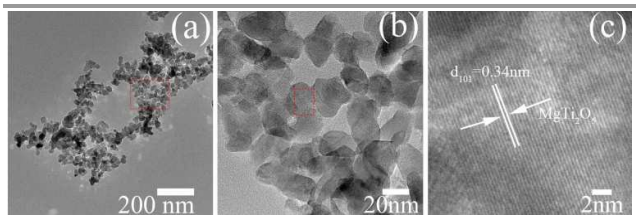


Figure 3. TEM (a and b) and HRTEM (c) images of PMT.

The morphology of PMT is nanocrystallines with small size TEM and HRTEM images in Figure 3a-c show the nanocrystallines are uniform, well dispersed and the average size is about 20-30 nm. The aggregated nanoparticles form many pores which enhance the surface area and are beneficial to photocatalysis. It is well known that the photocatalytic performance is related to the BET surface areas. The N_2 adsorption-desorption isotherms and the corresponding BJH pore size distribution plots of pure $MgTi_2O_5$ nanocrystals and commercial $MgTi_2O_5$ were performed, as shown in Figure S4. The BET surface areas for the prepared and pure $MgTi_2O_5$ nanocrystals, mixed phase $MgTi_2O_5/MgTiO_3$ and commercial $MgTi_2O_5$ are 64.94, 69 and 2.95 m^2/g, respectively. HRTEM image clearly shows the interplanar spacing of 0.34 nm that corresponding to the (101) plane of $MgTi_2O_5$. The high quality crystallinity and the pure phase are positive to charge transfer and separation.[19-21]

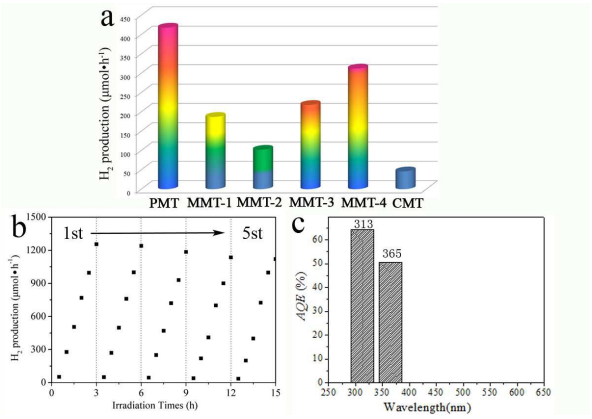


Figure 4. Photocatalytic H_2 production of different samples (a), time depend H_2 evolution and cycle experiment (b) and apparent quantum efficiency (c) of PMT.

The as-prepared magnesium titantes are regarded as potential photocatalyst for H_2 evolution. Figure 4a shows that the H_2 evolution over the prepared pure phase $MgTi_2O_5$, mixed-phase $MgTi_2O_5/MgTiO_3$, and commercial $MgTi_2O_5$ under UV light irradiation. It can clearly learn that pure phase $MgTi_2O_5$ (PMT) display the highest H_2 evolution efficiency, which is up to 418 μmol h^{-1} (average in three hours), much higher than that of mixed-phase ones and commercial one. It is important that the samples with different surface area play significant roles, compared with PMT and CMT. However, the surface area of PMT and MMT-4 are similar, but the efficiency is much different, which means there are also other factors affecting the activity. Time depended H_2 evolution curve in Figure 4b show the pure phase $MgTi_2O_5$ could sustainable produce H_2 along with the times. After five times recycle, the photocatalyst remain the catalytic efficiency with decline about only 10%. This illustrates the pure phase $MgTi_2O_5$ possess of high H_2 production efficiency and stability. The crystal structure didn't changes after five time recycles which can be learn from the XRD pattern in Figure S5.

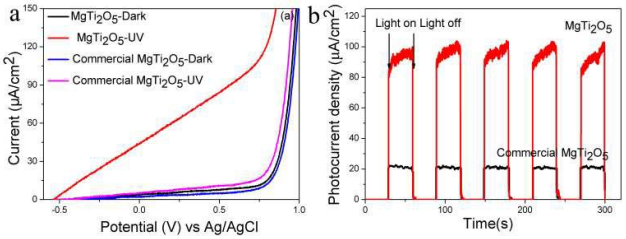


Figure 5. Liner sweep voltage (a) and transient photocurrent (b) of pure phase $MgTi_2O_5$ (PMT) and commercial $MgTi_2O_5$ (CMT).

In order to demonstrate the relationship of light energy and efficiency, we test and calculate the apparent quantum efficiency of the $MgTi_2O_5$ nanocrystals, which is 62.5% and 50.6% at 313 nm and 365 nm, respectively. It is in assistant with the UV-vis absorbance as shown in Figure 4c. This means the pure phase $MgTi_2O_5$ in this work is UV response photocatalysts and UV light is dominant of the photocatalytic efficiency. Significantly, the "solar-to-hydrogen" conversion efficiency (STH) of $MgTi_2O_5$ is 0.52%, which the computing method are followed by the previous report. [22]

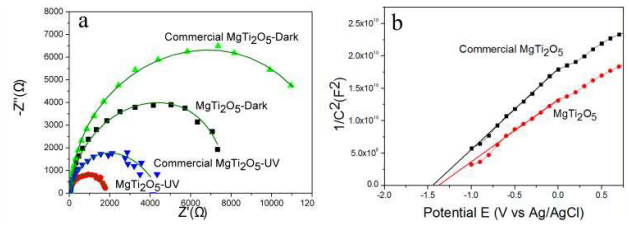


Figure 6. EIS and Matt-Schottky curves of pure phase $MgTi_2O_5$ (PMT) and commercial $MgTi_2O_5$ (CMT).

Photoelectrochemical (PEC) performance is a useful technique to demonstrate the charge separation and estimate the property of water splitting.[23,24] The PEC properties of PMT are also performed, CMT is utilized for contrast. Linear sweeps voltammogram of the $MgTi_2O_5$ materials shows a photocurrent density of 103 μA cm^{-2}, which is almost four times higher than that of the commercial $MgTi_2O_5$ materials (21 μA cm^{-2}) under UV light irradiation, as shown in Figure 5a. To further investigate the photocurrent response of PMT and CMT, the transient photocurrents of the samples were carried out during repeated ON/OFF illumination cycles at 0.7 V (vs.Ag/AgCl). Both of the samples show prompt and reproducible photocurrent responses upon each illumination (Figure 5b). The transient photocurrent density of PMT is 100 μA cm^{-2}, which is greatly enhanced compared to those of CMT (20 μA cm^{-2}). The transient photocurrent responses well match the linear sweeps voltammogram and display the stability of magnesium titanates materials.

The photogenerated charge transfer and separation need to overcome impedance of the interface.[25, 26] The electrochemical impedance measurements show smaller interfacial resistance for PMT than that of CMT, not only in dark but also under illumination, indicating a more efficient charge separation (Figure 6a). Mott-Schottky plots could reflect the type of semiconductors, the flat band and the charge density. Figure 6b demonstrates that both PMT and CMT are n-type semiconductors from a positive slope. The slope of the plot is inversely proportional to the charge density, the smaller it is, the higher of the charge density. The PMT showed a substantially smaller slope of the Mott-Schottky plot than CMT, illustrating PMT possess of higher charge density. Thus, PMT have smaller interface impedance and higher charge density, and also higher photocurrent density. These results give the bright evidence that PMT is beneficial for charge transfer and separation, may owing to the pure phase crystal structure and large surface area. Based on the results above, we speculate the enhancement is caused by (i) the pure phase structure that the effect of the harmful impurities of TiO_2 or Mg_2TiO_4 (mismatched electronic band structure) are eliminated; (ii) the large surface area due to the small nanoparticles compared with commercial one; (iii) maybe it is concerned with the defects because many nanomaterials have more or less defects but we have no directly evidence. However, it is believed this topic of defect in pure phase materials would inspire ones interesting to focus on the deep mechanism.

Conclusions

In summary, we successfully synthesized pure phase $MgTi_2O_5$ nanocrystals *via* a facile organic ligands coordinated polymerization method and followed by calcination in air. The pure phase could control by the concentration of metal ions. The lower concentration, the easier pure phase could be obtained. The pure phase materials show excellent photocatalytic hydrogen production activity because of the pure phase crystal structure without impurity as well as the large surface area that contributes to charge separation, demonstrated by PEC. It is believed that the organic ligands coordinated polymerization method could extend to other pure phase titanates or even perovskite photocatalysts for high activity H_2 evolution or water splitting.

Acknowledgements

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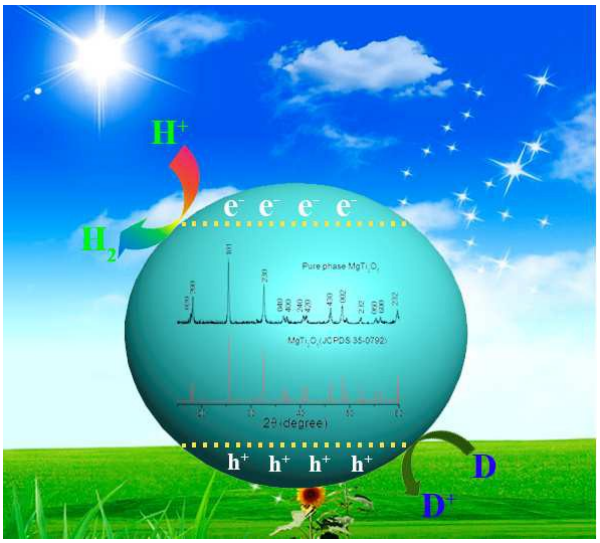

Undesirable phase transformation was overcome and pure phase $MgTi_2O_5$ nanocrystals with excellent photocatalytic H_2 production efficiency were facilely prepared.